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Electrochemical Study of Inhibition of Corrosion of Copper by Ofloxacin in Acid Media

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Abstract

The inhibition efficiency of ofloxacin, a fluoroquinolone on the corrosion of copper in acids has been studied employing polarisation, EIS and weight loss measurements. Ofloxacin exhibited good inhibition efficiency and the inhibition action was observed to be of mixed type, but with more of cathodic nature. Determination of Potential of zero charge established the mechanism of adsorption of the inhibitor onto the metal surface. From the temperature dependence of the corrosion rates, the activation energy (E_a) and the thermodynamic parameters such as the adsorption equilibrium constant (K_{ads}) and the free energy of adsorption (ΔG_{ads}) were calculated. The free energy of adsorption close to -40kJmol^{-1} indicates that the adsorption is through electrostatic coulombic attraction and chemisorptions, and it obeyed Langmuir adsorption isotherm. Among the potassium halides, only KI improved the inhibition efficiency of ofloxacin by synergism. The structural features obtained by quantum chemical calculations were also supportive of the experimental results.

Keywords : *Adsorption; Corrosion; Copper; Ofloxacin; Potentiodynamic polarisation; Thermodynamic properties.*

1. INTRODUCTION

Copper metal plays important roles in chemical and electronic fields due to its high electrical and thermal conductivity. Copper is one among the noble metals which require strong oxidants for its corrosion. The electrolytic plating and chemical dissolution are the main processes employed in the fabrication of electronic devices. The most widely used corrosive solution contains nitric acid, and hence it attracted a great deal of research on copper corrosion. The use of chemical inhibitors is one of the most practical methods for the protection against corrosion in acid medium.

In the present paper, inhibition efficiency of ofloxacin for corrosion of copper in 1.0M HNO_3 and 0.5M H_2SO_4 acid solutions were studied. Various techniques like electrochemical impedance spectroscopy, potentiodynamic polarisation, adsorption studies were performed. The different thermodynamic parameters were calculated and discussed.

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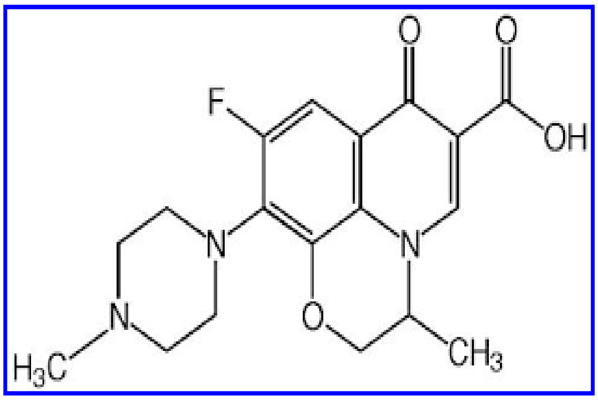

Fig. 1: Structure of ofloxacin.

2. EXPERIMENTS

2.1 Materials and reagents

Copper specimens of dimensions 2.5cm x 1cm x 0.1cm were used for weight-loss measurements. It has

a composition of 99.5 wt. % Cu, 0.003 wt. % Ni, 0.116 wt. % Si, 0.019 wt. % Al and 0.002 wt. % Mn. These specimens were polished using emery papers of different grades, washed with acetone and dried. A Teflon coated cylindrical copper electrode of previous composition was used for electrochemical studies. All the chemicals used were of analytical reagent grade (Sigma Aldrich) and E Merck (India). Inhibitor stock solutions of concentration 2.5 M were prepared with respective acids.

2.2 Weight loss measurements

The copper specimens, in triplicate, were immersed for 2 hrs in 100 ml of the acid media at room temperature in the blank and with the inhibitor. The average weight loss was used to calculate the inhibition efficiency employing the formula:

$$\mathrm{IE} = \left(\frac{W-W'}{W}\right) \mathrm{X}\ 100 \qquad (1)$$

Where W and W' represent the corrosion rates in the uninhibited and inhibited solutions respectively.

2.3 Electrochemical impedance measurements

A three electrode set up was used for electrochemical studies. A Pt foil is used as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and the Teflon coated copper rod as the working electrode. A stabilization period of 45 minutes was given, after immersion of the specimen in the corrosive media. Electrochemical Impedance measurements were carried out using a potentiostat (GAMRY REFERENCE 600) and the data were analyzed using Gamry Echem Analyst software. Inhibition efficiencies (IE%) were calculated using the expression (Doner *et al.* 2011)

$$IE\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} X100 \qquad (2)$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values in the uninhibited and inhibited solutions respectively.

2.4 Polarization measurements

Potentiodynamic polarization curves were recorded using the same cell setup at a potential sweep rate of 1.6 mVs^{-1}. The potentials were scanned primarily from negative potentials through OCP to the positive side and E_{corr} and i_{corr} values were derived from the polarisation curves. The inhibition efficiencies were calculated using the relationship (Sahin *et al.* 2002).

$$IE\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \mathrm{X}\ 100 \qquad (3)$$

where i_{corr} and i'_{corr} are the corrosion current densities in the blank and in the presence of inhibitor respectively.

2.5 Study of Synergistic effect of halide ions

The synergistic effect was studied using KCl, KBr, and KI. Aramki and Hackermann equation (Aramaki and Hackerman, 1969), was used to calculate S_θ as given below

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} \qquad (4)$$

Where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1= surface coverage by anion; θ_2 = surface coverage by cation; θ'_{1+2} = measured surface coverage by both cation and anion.

2.6 Determination of Activation energy

Potentiodynamic polarization studies were carried out in the presence and in the absence of the inhibitor in the temperature range 308K to 328K in both the acid solutions and the activation energy for the adsorption of the inhibitor onto copper surface was determined using the Arrhenius equation

$$i_{corr} = A\ e^{-Ea/RT} \qquad (5)$$

Where i_{corr} is corrosion current density, A is the Arrhenius pre-exponential constant, Ea is the energy of activation, R is universal gas constant, and T is the absolute temperature.

2.7Measurement of potential of zero charge

Electrochemical impedance values were recorded at 20 kHz AC frequency, after varying the applied DC potentials. The PZC was obtained from the lowest point of the plot of differential capacitance versus applied DC potential.

2.8 Surface morphology studies

The surface morphologies of the corroded samples in the blank and in the presence of the inhibitor were carried in a digital Scanning Electron Microscope. All micrographs were taken at a magnification of 200X.

2.9 Quantum chemical calculations

The structures were first optimized and the simulations were conducted to calculate the electronic parameters. The Quantum chemical calculations were done using Semi-empirical method - Parameterized Model 3 (PM3) (Gao, 1996). Density functional theory (DFT) (Geerlings *et al.* 2003) has been found to be successful in providing all the theoretical parameters.

3. RESULTS & DISCUSSION

3.1 Weight loss measurement

Table1 gives the inhibition efficiencies at different concentrations of the inhibitor. The inhibition efficiency was found to increase with concentration of the inhibitor, very steeply at the initial doses, but however tend to attain a steady value (Fig.1a, b) since an appreciable area of the surface gets covered by the inhibitor already by adsorption. The curve tends to flatten up with further increase, exibiting type I adsorption and about 90%inhibition is achieved at 1.0m M dose.

3.2 Electrochemical impedance study

Fig. 2a and 2b are the impedance spectra recorded in 1.0M nitric acid and 0.5 M sulphuric acid solutions at various concentration of the inhibitor. The occurrence of depressed semi circles is proposed to be due to the non-ideal capacitive behaviour at the electrochemical solid/liquid interfaces (Hosseini *et al.* 2003). This capacitance dispersion at the solid surfaces is mainly caused by its roughness, chemical inhomogeneities, degree of polycrystallinity and anion adsorption (Rahman *et al.* 1997). With the equivalent circuit given in the figure 3, the impedance spectrum which displays a high frequency capacitive loop and the Warburg impedance in the low frequency can be analyzed (Khaled, 2010; Ma *et al.* 2002).

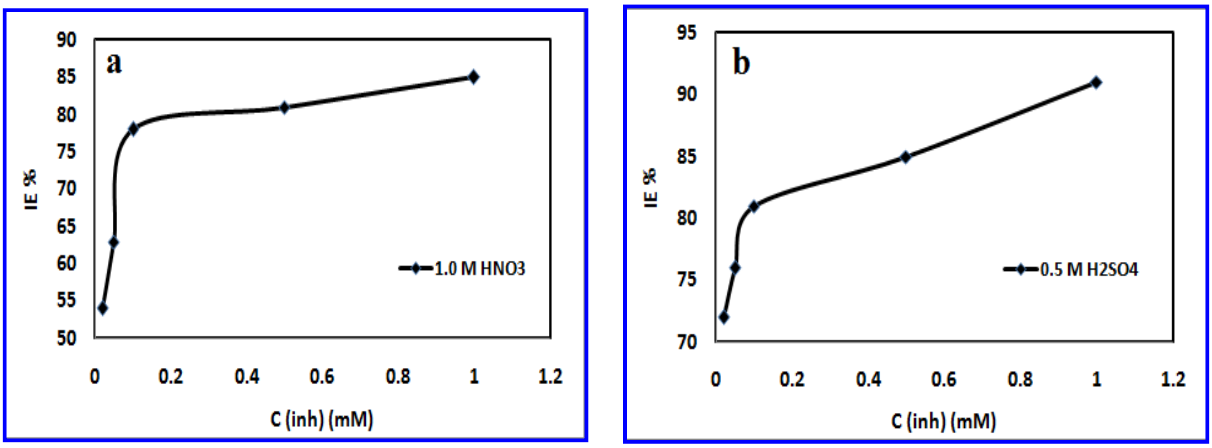

Fig. 1: Plots of inhibitor efficiency (%) with concentration of ofloxacin in (a) 1.0 M HNO_3 (b) 0.5M H_2SO_4 media

Table 1 Inhibitor efficiency from weight loss measurement for copper in 1.0M HNO_3 and 0.5M H_2SO_4 solutions at different concentration of the inhibitor

Medium	Inhibitor concentration (mM)	Corrosion rate (mmpy)	Inhibitor efficiency (IE%)
1.0 M HNO_3	Blank	47.2162	-
	0.02	21.5828	54.3
	0.05	17.4167	63.1
	0.1	10.5889	77.6
	0.5	9.1423	80.6
	1.0	7.0592	85.0
0.5M H_2SO_4	Blank	22.3929	-
	0.02	6.3649	71.6
	0.05	5.3233	76.2
	0.1	4.1661	81.4
	0.5	3.2981	85.3
	1.0	2.0830	90.7

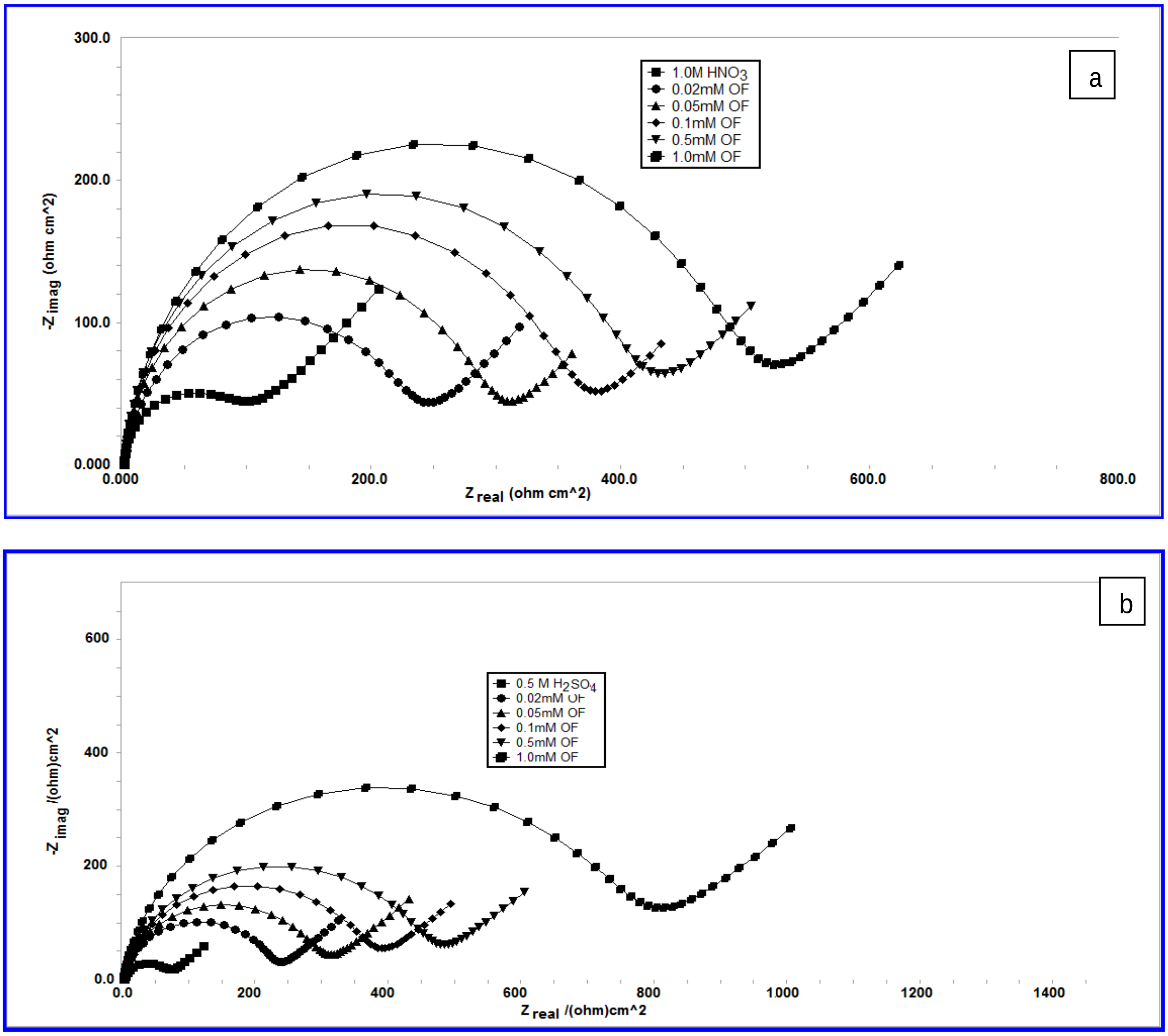

Fig. 2: The Nyquist plots for Cu electrode obtained in (a) 1.0M HNO_3 (b) 0.5M H_2SO_4 solution at various concentrations of ofloxacin

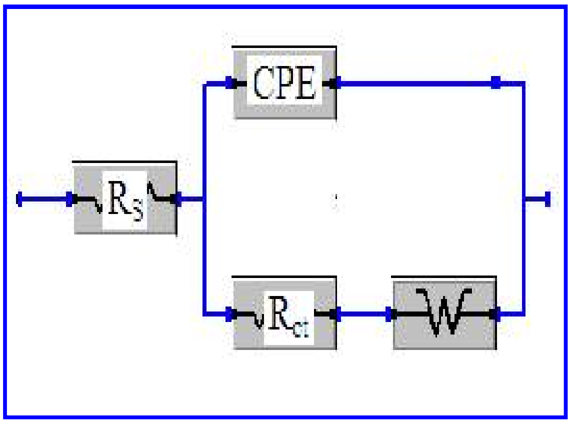

Fig. 3: Randles Equivalent Circuit for the corrosion of copper in acid media.

Angular frequency and C_{dl} are calculated using the following equation (Hsu and Mansfeld, 2001).

$$\omega_{max} = \left(\frac{1}{R_{ct}Y_0}\right)^{1/n} \tag{6}$$

$$C_{dl} = Y_0\,(\omega_{max})^{n-1} \tag{7}$$

The R_{ct} values increased with increase in inhibitor concentrations, whereas the values of C_{dl} decreased in both the media. Increase in the R_{ct} is due to the increase in the surface coverage by the inhibitor. The decrease in C_{dl} is a result of the adsorption of the inhibitor molecule with water replacement at the metal/ solution interface and decreased the rate of corrosion (Benabdellah *et al.* 2007).

Table 2. Electrochemical parameters derived from EIS measurements for the corrosion of copper in 1.0M HNO_3 and 0.5M H_2SO_4 solutions at different concentration of the inhibitor.

Medium	Inhibitor Concentration (mM)	R_{ct} Ωcm^2	Y_0 (X 10^{-6}) $\Omega^{-1}cm^{-2}$	n	C_{dl} μFcm^{-2}	Inhibitor Efficiency (IE%)
1.0M HNO_3	Blank	87.0	862.0	0.99	146	-
	0.02	223.7	366.2	0.93	102	61
	0.05	286.0	308.2	0.96	89	70
	0.10	351.0	265.2	0.96	75	75
	0.50	398.0	179.7	0.95	58	78
	1.0	487	128.4	0.94	49	82
0.5M H_2SO_4	Blank	63.0	330.0	0.93	159	-
	0.02	221.0	93.4	0.91	118	72
	0.05	290.5	90.7	0.92	91	78
	0.10	362.0	89.0	0.92	73	83
	0.50	451.9	92.0	0.94	51	86
	1.0	749.1	70.2	0.92	24	92

3.3 Polarization measurements

The influence of the inhibitor on the anodic and cathodic Tafel slopes, are shown in the potentiodynamic polarization curves presented in Fig 4a and 4b. However, the influence was more significant in the cathodic curve. The cathodic polarization curves are almost parallel to each other, indicating that the hydrogen evolution is under activation control (Zarrouk *et al.* 2012). According to Corrosion theories (Barcia *et al.* 1993), (Barcia and Mattos, 1990) the rightward shift of the cathodic curves reveal that the corrosion is mainly accelerated by cathodic reactions. Generally if the shift in E_{corr} is greater than 85 mV with respect to E_{corr} of uninhibited solution, the inhibitor can be viewed as either cathodic or anodic type (Li *et al.* 2008; Li *et al.* 2009; Ferreira *et al.* 2004). In the present study the maximum shift of E_{corr} is less than 85mV in the presence of inhibitor in both the media, and hence the inhibitor can be considered as mixed type (Zarrouk *et al.* 2012).

No passive film is formed on the copper surface since no steep slope is found in the anodic range in the polarization curves. In deaerated acid solutions, Cu^{+2} was not observed but Cu dissolves in the presence of dissolved oxygen forming Cu^{+2}ion by the following mechanism

Anodic reaction:

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad (8)$$

Cathodic reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (9)$$

The diffusion of soluble Cu^{+2} species from the outer Helmhotz plane to the bulk solution (Ferreira *et al.* 2004) controlled the dissolution of copper.

Table 3 indicates that β_c and βa change with increase in inhibitor concentration, and the higher β_c indicates its greater influence on the retardation of cathode reaction than the anodic reaction. (Sanghvi *et al.* 1997). This indicated that the ofloxacin reduces the cathodic reaction to a larger extent than the anodic reaction.

3.4 Mechanism of adsorption

An organic compound (org_{sol}) from the aqueous medium displaces the water molecules associated with the metal surface (H_2O_{ads}) during the adsorption of inhibitor molecules at the metal solution interface.

$$Org_{(sol)} + xH_2O_{ads} \rightarrow Org_{ads} + xH_2O \qquad (10)$$

Where ‘x’ indicates the number of water molecules displaced by one ofloxacin molecule. The surface coverage (θ) of the inhibitor was calculated using the relation,

$$\theta = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \qquad (11)$$

Where R'_{ct} and R_{ct} are the charge transfer resistance values in the inhibited and uninhibited solutions respectively. Analysis showed that the adsorption followed Langmuir isotherm, given by the expression (Zarrouk *et al.* 2012; Joseph and Joseph, 2011),

$$C_{inh}/\theta = C_{inh} + 1/K_{ads} \qquad (12)$$

and the plots are shown in fig 5. Where C_{inh} is the concentration of the inhibitor, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant. At constant temperature, the value of K_{ads} is determined from the plot of C_{inh} vs C_{inh}/θ. The standard free energy of adsorption is calculated using the expression:

$$K_{ads} = 1/55.5 \exp^{-\Delta G/RT} \qquad (13)$$

Where ΔG is the free energy of adsorption, T is the temperature, R is the universal gas constant, and 55.5 is the concentration of water in mol L^{-1}. The plots obtained were linear with correlation coefficients greater than 0.9. The calculated values of ΔG_{ads} at room temperature in 1.0M nitric acid and 0.5 M sulphuric acid solutions are -39.15kJmol^{-1} and -42.84kJmol^{-1} respectively. The negative values of ΔG_{ads} show the spontaneous adsorption of ofloxacin molecules onto the metal surface. In general -ΔG_{ads} less than and around 20 kJ mol^{-1} represents physisorption, while a value greater than 40kJmol^{-1}represents chemisorption. If -ΔG_{ads} lies between 20kJmol^{-1} and 40kJmol^{-1}, it represents both physisorption and chemisorption (Joseph and Joseph, 2011; Yurt *et al.* 2005; Quraishi *et al.* 2000). Thus, in the present study, the ofloxacin molecules get adsorbed onto the metal surface by both types of adsorptions, but with a higher contribution from chemisorption (Bentiss *et al.* 1999).

Table 3. Electrochemical parameters for the corrosion of copper in 1M HNO_3 and 0.5M H_2SO_4 solutions at different concentration of the inhibitor, derived from Tafel polarization curves.

Medium	Concentration (mM)	E_{corr} (mV)	i_{corr}(μA cm^-2)	β_cx10^{-3} (V)	β_ax10^{-3} (V)	Corrosion rate(mpy)	IE%
HNO_3	Blank	42.10	116	429.5	67.74	187.8	-
	0.02	-3.28	34.4	259.5	60.70	55.67	70
	0.05	-0.69	30.0	308.9	55.10	48.51	74
	0.1	-1.08	25.2	282.7	60.00	40.75	78
	0.5	-3.03	21.5	244.8	51.00	34.92	81
	1.0	-14.3	18.2	226.4	59.92	29.48	84
H_2SO_4	Blank	4.52	172.0	714.3	84.67	81.35	-
	0.02	-11.90	25.2	666.3	43.30	40.75	85
	0.05	-18.30	21.5	527.1	45.10	34.92	87
	0.1	-18.90	15.1	430.7	50.50	24.47	91
	0.5	-18.90	9.82	407.8	45.80	15.89	94
	1.0	-22.44	6.91	358.8	45.21	11.78	96

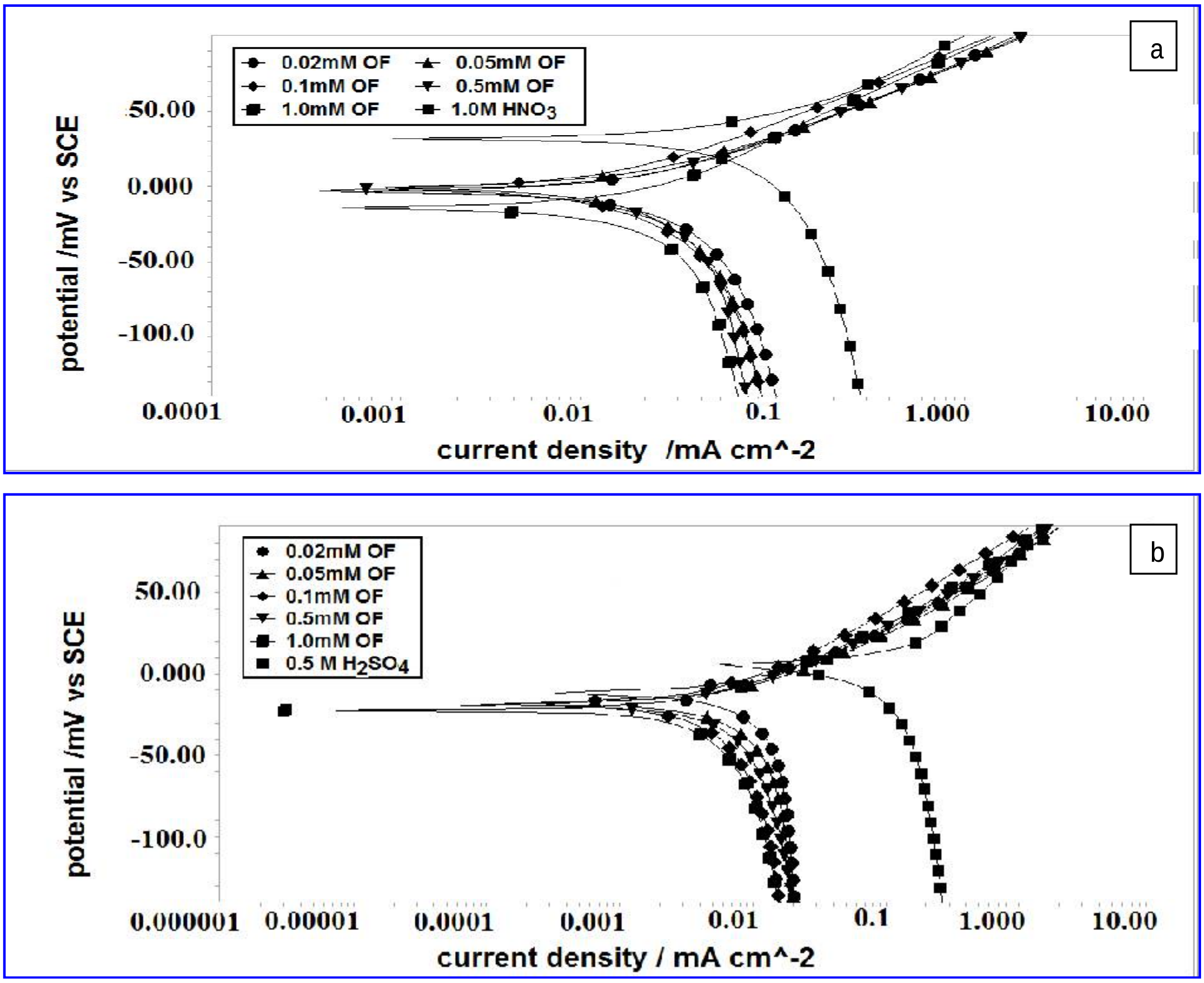

Fig. 4: Tafel plots for Cu in (a) 1.0M HNO_3 (b) 0.5M H_2SO_4 solution at various concentrations of Ofloxacin

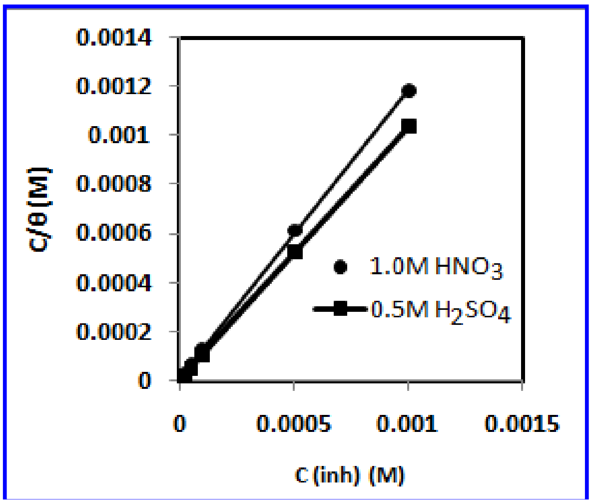

Fig. 5: Langmuir Adsorption Isotherm for the adsorption of ofloxacin onto copper surface in 1.0M HNO_3 and in 0.5M H_2SO_4 solutions.

Table 4 shows that the inhibitor efficiency increases, but at the same time, corrosion rate also increases with increase in temperature.

The Arrhenius plots and Transition state plots are shown in Fig. 6 and 7. Inspection of Table 5 shows that the values of E_a determined in the presence of ofloxacin are lower than that in the uninhibited solution. This is an indication of decrease in energy barrier for the adsorption of the inhibitor molecules onto copper surface. The surface area covered by the inhibitor molecule increases with increase in temperature and the metal dissolution rate in the corrosive media is controlled by diffusion of the corrosion product through the protective film of the inhibitor molecule (Szauer and Brandt, 1981). The decrease in E_a with the addition of inhibitor in both the media reveals that the inhibitor molecules are adsorbed onto the metal surface by chemisorptions (Szauer and Brandt, 1981; Ivanov, 1986; Ma *et al.* 2003). The adsorption is an exothermic process since ΔH is negative.

Table 4. Electrochemical parameters from Tafel polarization curves for the corrosion of copper in 1.0M HNO_3 and 0.5M H_2SO_4 solution at different temperatures

Medium	Conc. (mM)	Temperature (K)	E_{corr} (Mv)	i_{corr} µA cm^{-2}	β_C X10^{-3} V	β_a x10^{-3} V	Corrosion rate (mpy)	IE%
HNO_3	Blank	308	2.59	30.3	173.6	54.40	49.04	-
	Blank	318	10.80	199.0	411.4	65.70	322.6	-
	Blank	328	21.70	358.0	440.0	59.90	579.2	-
	1mM	308	-23.40	10.8	182.1	48.10	17.43	64
	1mM	318	-3.44	22.9	174.9	45.40	36.99	88
	1mM	328	12.70	50.6	163.1	56.40	81.70	86
H_2SO_4	Blank	308	-14.00	12.2	537.3	49.10	19.82	-
	Blank	318	-46.67	30.4	281.0	50.23	49.19	-
	Blank	328	11.70	88.5	271.9	62.89	143.2	-
	1mM	308	-38.53	5.696	189.9	52.36	9.217	53
	1mM	318	-38.58	6.777	223.2	48.71	10.97	78
	1mM	328	-1.356	24.01	586.4	59.35	38.75	73

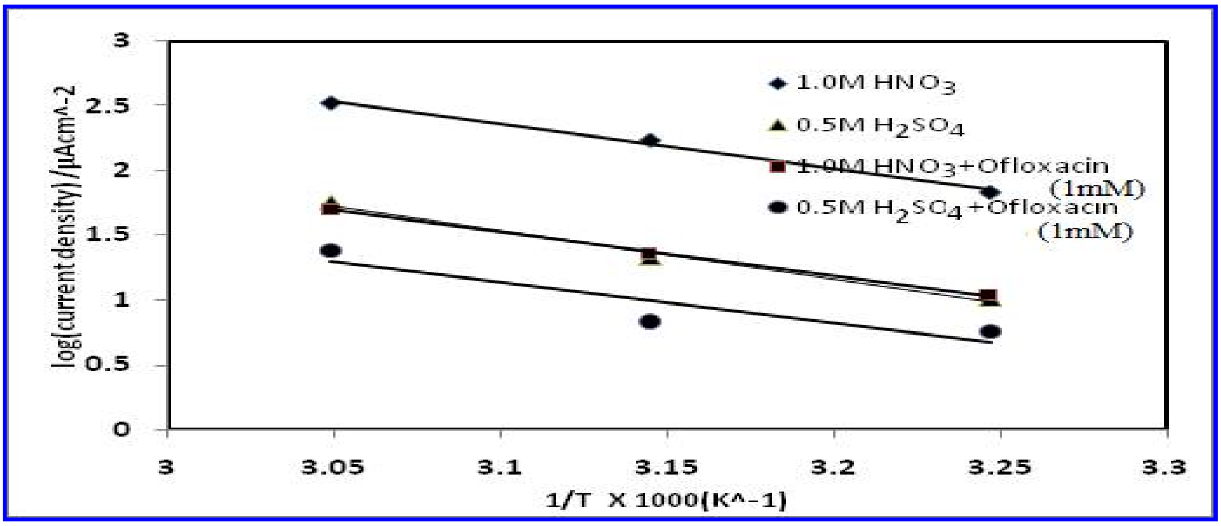

Fig. 6: Typical Arrhenius plots for corrosion of Cu in 1.0M HNO_3 and in 0.5M H_2SO_4 solution

Table 5. Thermodynamic parameters obtained from potentiodynamic polarization studies

Medium	Inhibitor concentration	K_{ads} (M^{-1})	ΔG_{ads} KJ/mole	ΔH KJ/mole	ΔS J/mole/K	E_a (KJ / mole)	R
HNO_3	Blank	-	-	-63.7	-26.8	66.44	0.993
	0.5mM OF	117785	-39.14	-62.2	-28.3	64.81	0.998
H_2SO_4	Blank	-	-	-69.5	-38.2	72.19	0.989
	0.5mM OF	518000	-42.84	-57.4	-45.4	59.94	0.826

The adsorption of organic compounds onto metal surfaces generally depends on the surface charge of the metal and the charge or dipole moment of the inhibitor molecule and other ions that are specifically adsorbed onto the metal surface (Quraishi *et al.* 2000). The surface charge of the metal is determined using the open circuit potential and PZC values (Saliyan and Adhikari, 2008). The dependency of the double layer capacitance on the DC potential is shown in the figures 8(a)-(d). Table 6 gives the E_{ocp} and PZC data.Using the equation below, the surface charge on copper at the open circuit potential is calculated.

$$E_r = E_{ocp} - E_{pzc} \quad (14)$$

Where E_r is antropov's rational corrosion potential (Popova *et al.* 2003). The surface charge of copper at the OCP was found to be positive in the inhibited and uninhibited sulphuric acid and nitric acid solutions. Hence the the sulphate and nitrate ions will first get adsorbed onto the metal surface (Ma *et al.* 2003; Solmaz *et al.* 2008; Saliyan and Adhikari, 2008; Popova *et al.* 2003), and the protonated inhibitor molecules make bond with the anions and retard the metal dissolution (Doner *et al.* 2011).

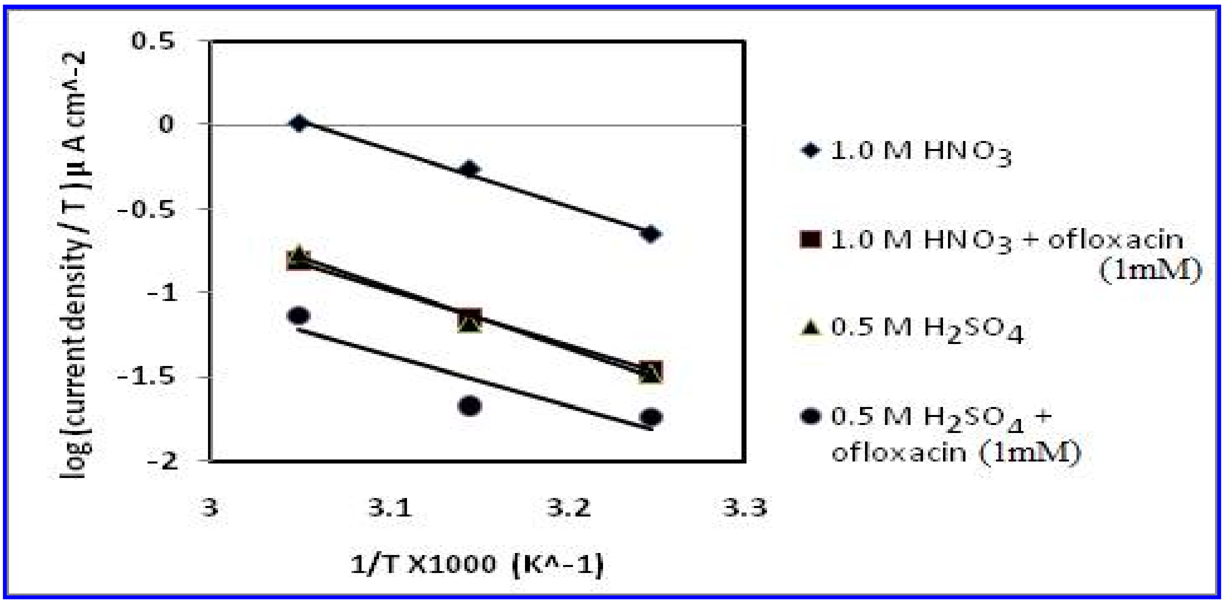

Fig. 7: The transition state plots for corrosion of Cu in 1.0M HNO_3 and in 0.5M H_2SO_4 solution

Table.6 Excess charge on Cu electrode in 1.0M HNO_3 and 0.5M H_2SO_4 solutions

Medium	E_{OCP}(mv/SCE)	PZC(mv/SCE)	Excess charge E_{OCP}-E_{PZC}
1.0M HNO_3	42.10	+40	+2.1
1.0M HNO_3+0.5mM of inhibitor	-3.03	-220	+217
0.5M H_2SO_4	+4.52	-20	+24.52
0.5MH_2SO_4+0.5mM of inhibitor	-18.95	-20	+1.05

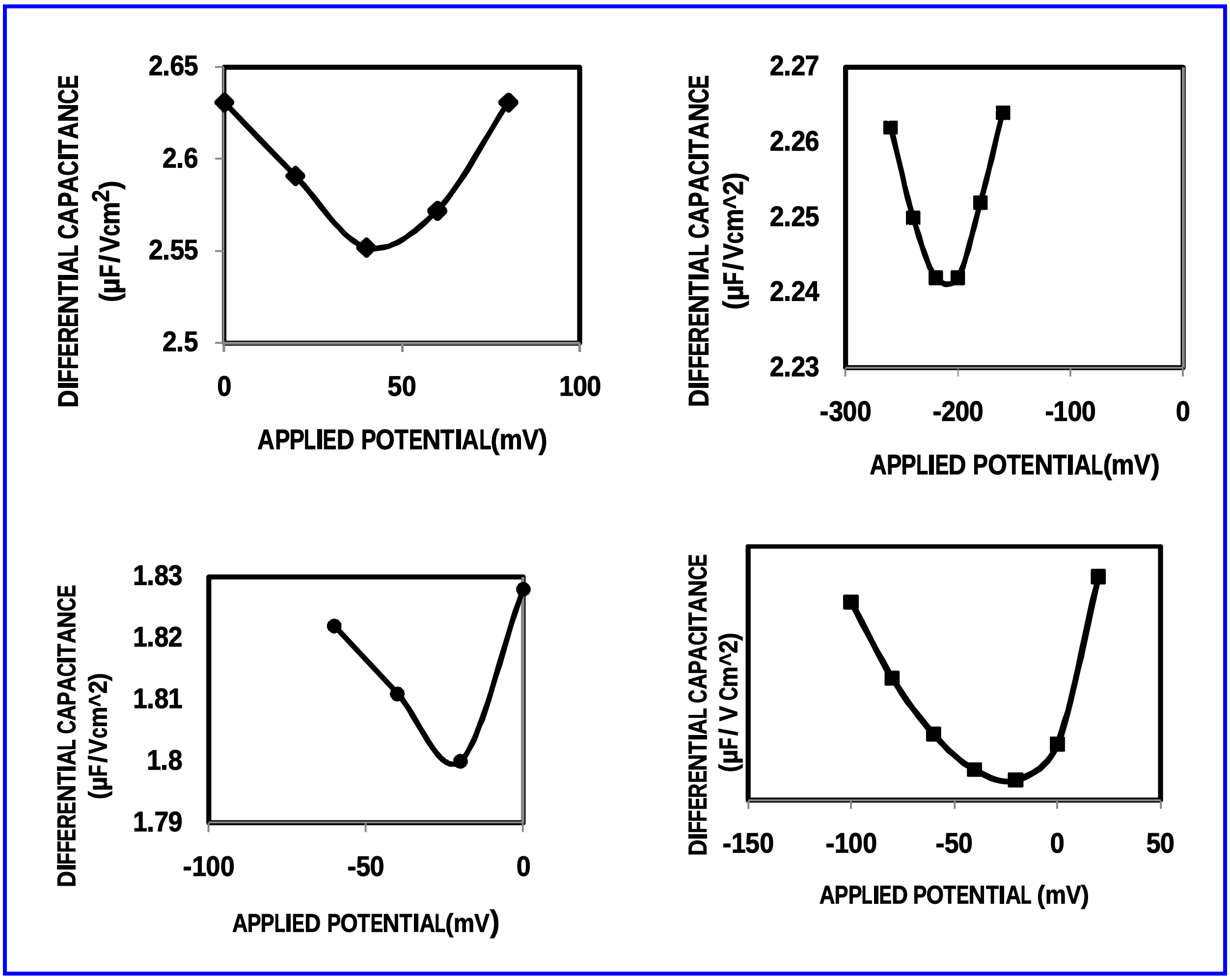

Fig. 8: The plot of differential capacitance vs. applied electrode potential for copper in (a) 1.0M HNO_3 solution (b) 1.0M HNO_3 containing 0.5mM ofloxacin(c) 0.5 M H_2SO_4(d) 0.5M H_2SO_4 containing 0.5mM ofloxacin.

3.5 Synergistic effect of halide ions

When two or more corrosion inhibitors are present in a corrosive environment, the inhibitor efficiency might be greater due to synergy rather than a mere additive effect.

Since the surface charge of copper was positive, it is proposed that the halide ions will first get adsorbed onto the metal surface (Solmaz *et al.* 2008; Saliyan and Adhikari, 2008; Popova *et al.* 2003) and the protonated inhibitor molecules get adsorbed on the anions and retard the metal dissolution (Doner *et al.* 2011) as given in the equations 15 and 16.

$$X^{-}_{S} \rightleftharpoons X^{-}_{ads} \quad (15)$$

$$X^{-}_{ads} + HI^{+}_{S} \rightarrow (X^{-}\text{-}HI^{+})_{ads} \quad (16)$$

Thus the halide ions improve adsorption of the inhibitor by forming intermediate bridges between metal surface and the organic inhibitor (Ozcan *et al.* 2008; Zhao and Chen, 2012; Feng *et al.* 1999; Obot *et al.* 2009; Umoren *et al.* 2010; 2008; Pavithra *et al.* 2010; Ai *et al.* 2006). Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the halide anions. The synergism parameters S_θ obtained from the impedance studies on addition of KCl, KBr, and KI are given in the Table 7.From the table, it was found that synergistic effect was exhibited by iodide ion whereas chloride and bromide ions exhibit antagonistic effect in both the acid media. It is due to large ionic radius, low electronegativity and high hydrophobicity of the iodide ions (Bentiss *et al.* 2002) when compared to other halide ions, which enhances the adsorption of the inhibitor molecules onto the metal surface (Saliyan and Adhikari, 2008).

Table 7. Electrochemical parameters derived from EIS studies for the corrosion of copper in 1M HNO_3 and 0.5M H_2SO_4 solutions in the presence of KCl, KBr and KI

Medium	Inhibitor Concentration (mM)	Y_0 (X 10^{-6}) $\Omega^{-1}cm^{-2}$	n	R_{ct} Ωcm^2	θ	S_θ
1.0M HNO_3	Blank	862.9	0.997	87	-	-
	0.1mM OF	265.2	0.961	351	0.7521	-
	0.5mM KCl	189.1	0.898	313	0.7220	-
	0.1mM OF + 0.5mM KCl	120.2	0.926	198	0.5606	0.1568
	0.5mM KBr	271.0	0.912	231.8	0.6246	-
	0.1mM OF + 0.5mM KBr	149.4	0.939	622.9	0.8603	0.6657
	0.5mM KI	99.5	0.905	123	0.2926	-
	0.1mM OF + 0.5mM KI	55.30	0.906	1158	0.9248	2.33
0.5M H_2SO_4	Blank	330	0.930	63	-	-
	0.1mM OF	79.4	0.927	362	0.8259	-
	0.5mM KCl	349.1	0.945	191	0.6701	-
	0.1mM OF + 0.5mM KCl	80.9	0.926	215.9	0.7081	0.1966
	0.5mM KBr	256.7	0.934	154	0.5909	-
	0.1mM OF + 0.5mM KBr	84.5	0.937	584.6	0.8922	0.6604
	0.5mM KI	152.6	0.926	174	0.6379	-
	0.1mM OF + 0.5mM KI	45.1	0.962	2390	0.9736	2.38

3.6 Surface morphology

Fig. 9a and 9b are the SEM of copper specimen exposed to the acid solutions. These pictures show the existence of pits due to corrosion of copper in acid media. The SEM after the addition of 0.5mM ofloxacin to the corrosive media are shown in Fig. 9c and 9d. There is no pit formation in these pictures which is due to the protection provided by the adsorption of inhibitor molecules onto the metal surface.

3.7 Quantum chemical studies

Table 8 presents the calculated theoretical parameters which provide information about the reactive behaviour of the inhibitor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule. Therefore, higher the values of E_{HOMO}, better is the tendency towards donation of electrons enhancing the adsorption of the inhibitor on metal surface leading to better inhibition efficiency (Bouklah *et al.* 2012). On the otherhand, E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface thus increases with increasing HOMO and decreasing LUMO energy values. The low ionization energy 8.8950 (eV) of ofloxacin supports its observed higher efficiency. With the softness value of 0.25100(eV) and with low hardness value of 3.98400 (eV), Ofloxacin has good inhibition efficiency.

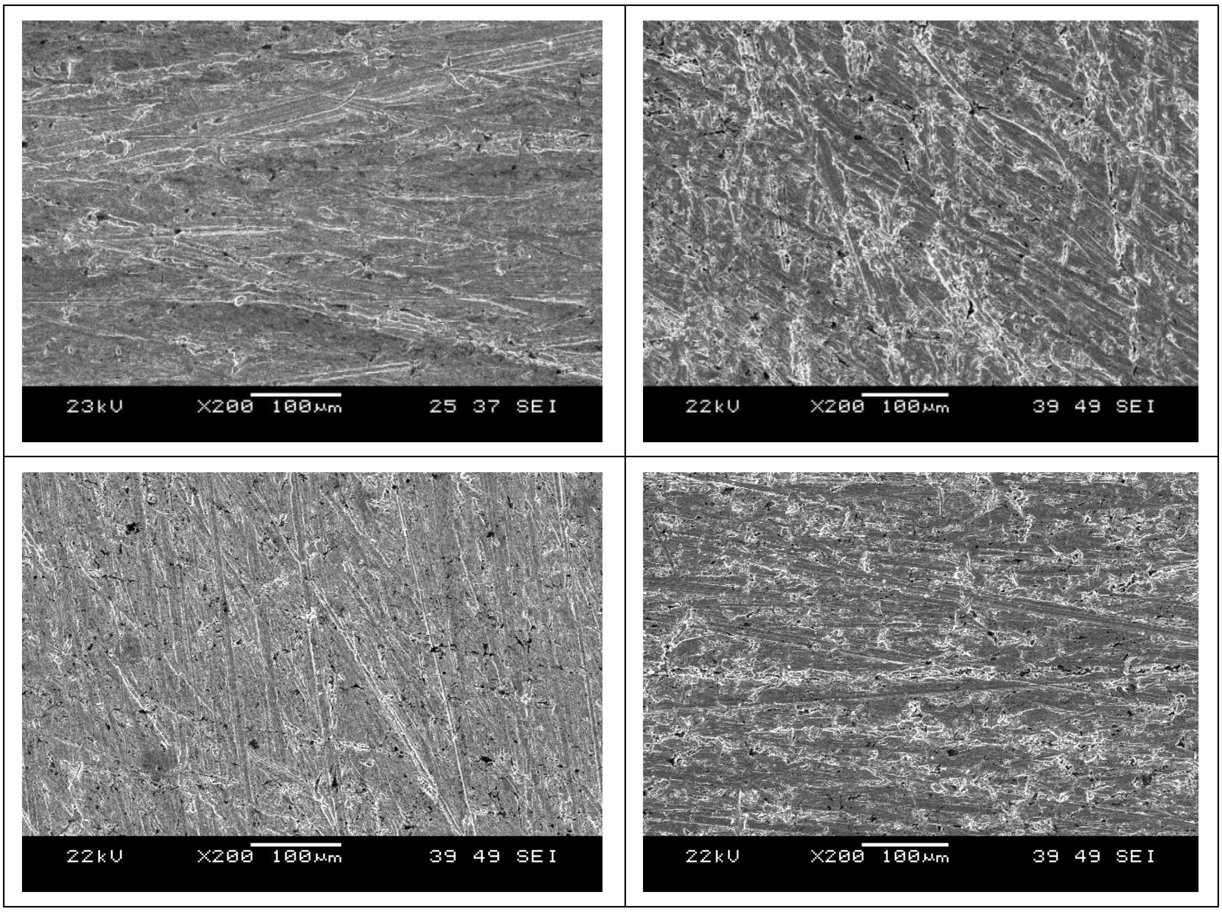

Fig. 9: SEM of copper specimen (a)after immersion in 1.0M HNO_3(b) after immersion in 0.5M H_2SO_4, (c) after immersion in 1.0M HNO_3 containing ofloxacin,(d) after immersion in 0.5M H_2SO_4 containing ofloxacin

Table 8. Quantum chemical parameters of Ofloxacin

Total energy (E) (ev)	-3923.61018
Electronic energy(ev)	-30377.32
HOMO(ev)	-8.895
LUMO(ev)	-0.823
Energy gap(ev)	8.072
Ionisation potential I(ev)	8.895018
Electron affinity(ev)	0.823
Electronegativity χ (ev)	4.807009
Dipole moment μ	-4.807009
Hardness η (ev)	3.984009
Softness σ (ev)	0.251003449
Electrophilicity ω (ev)	2.90000
ΔN	-0.0415

4. CONCLUSION

(i) The results show that the inhibitor efficiency increases with increase in ofloxacin concentration and ofloxacin can act as a good inhibitor for the corrosion of copper in both acid media.

(ii) EIS studies reveal that these molecules get adsorbed onto the metal surface by replacing water molecules and act as a diffusion barrier.

(iii) The potentiodynamic polarization studies reveal that ofloxacin acts as a mixed type of inhibitor.

(iv) The adsorption of ofloxacin obeys Langmuir adsorption isotherm. The negative ΔG_{ads} values indicate that the adsorption is spontaneous.

(v) The adsorption is through chemisorption since the value of free energy of adsorption is very close to -40kJmol^{-1}

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